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Local-density-functional total energy gradients in the linear-combination-of-Gaussian-type-orbitals method

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I. INTRODUCTION

Accurate local density functional (LDF) gradients require corrections for the fact that the orbital basis set is finite[1-8] and that the local one-electron potential is treated using a finite basis set[5-8]. The linear combination of Gaussian-type orbitals (LCGTO) local density functional (LDF) approach to molecules[9], polymers[10], and slabs[11] is well established. For these lower-dimensional systems that are not periodic in three dimensions, Fourier-transform methods cannot be used to readily compute gradients of the total energy (for a fixed number of plane waves), unless one uses supercell calculations (which are singular in the separate fragment limit for a fixed number of plane waves). If an LDF such as $X\alpha$ lends itself to an analytical LCGTO treatment—i.e. three-dimensional numerical integrations or fits can be avoided—then accurate gradients could be computed given a converged self-consistent-field (SCF) LDF LCGTO total energy[5]. In order to be able to use any LDF, a number of workers have recently implemented methods for computing the gradients of the molecular total energy that take into account the fact that the orbital basis set is finite and that the electronic Coulomb potential, the largest part of the one-electron potential, is treated using a finite expansion[6-7]. For a different purpose Averill and Painter[12] have considered fitting the density using the LCGTO LDF total energy and computed exact gradients including the effects of the density fit, assuming an exact three-dimensional numerical integration of the exchange-correlation (xc) forces. We consider herein the effects of approximating the xc energy density using a necessarily inexact fit to an LCGTO sum and the use of three-dimensional numerical integration techniques in the fitting scheme on the evaluation of a gradient with respect to nuclear coordinates of the LCGTO-LDF total energy expression.

II. PRELIMINARIES

The nonrelativistic total energy and one-electron molecular orbitals, in the electric field caused by nuclei of charges Z_k at positions $\mathbf{R}_i$, are determined by variational minimization of the LDF total-energy expression,

$$E = \sum_{k>k'} \frac{Z_k Z_{k'}}{|\mathbf{R}_k - \mathbf{R}_{k'}|} - \frac{1}{2}\sum_i \int d^3r\, n_i\, \phi_i(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$$
$$- \sum_k Z_k \left\langle \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} \right\rangle + \frac{[\rho|\rho]}{2} + \langle \rho(\mathbf{r}) U_{xc}(\rho(\mathbf{r})) \rangle \,, \tag{1}$$

where both $\langle f(1) \rangle$ and $\langle f \rangle$ are compact notation for $\int d^3r f(\mathbf{r})$, and where $[f_1|f_2]$ is compact notation for $\int d^3r_1 \int d^3r_2 f_1(\mathbf{r}_1) f_2(\mathbf{r}_2)/r_{12}$. In this expression the ϕ_i are the one-electron molecular orbitals and $\rho(\mathbf{r})$,

$$\rho(\mathbf{r}) = \sum_i n_i\, \phi_i^*(\mathbf{r})\, \phi_i(\mathbf{r}), \tag{2}$$

is the charge density when the ith molecular orbital is occupied by n_i electrons. (This work will not consider the case where there is net spin polarization of the electrons, the generalization to such a case is straightforward.) The one-electron molecular orbitals are expressed in LCGTO fashion,

$$\phi_i(\mathbf{r}) = \sum_j c_{ji} \chi_j(\mathbf{r}), \tag{3}$$

and satisfy the LDF one-electron secular equation,

$$\sum_j \left\langle \chi_{j'} \left| -\tfrac{1}{2}\nabla^2 - \sum_k \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|} + V_{es}(\mathbf{r}) + V_{xc}(\rho(\mathbf{r})) \right| \chi_j \right\rangle c_{ji} = \sum_j \langle \chi_{j'} | \chi_j \rangle\, c_{ji} \epsilon_i \tag{4}$$

Relating the total energy and the one-electron equations are the electrostatic potential due to all electrons,

$$V_{es}(\mathbf{r}) = \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{5}$$

and the local one-electron xc potential,

$$V_{xc}(\mathbf{r}) = \frac{d[\rho(\mathbf{r})U_{xc}(\rho(\mathbf{r}))]}{d\rho(\mathbf{r})} = U_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r})\frac{dU_{xc}(\rho(\mathbf{r}))}{d\rho(\mathbf{r})}. \tag{6}$$

This expression can be inverted to give the density derivative of the xc energy operator,

$$\frac{dU_{xc}}{d\rho} = \frac{V_{xc} - U_{xc}}{\rho}. \tag{7}$$

Initially, we follow the suggestion of Sambe and Felton[13] and approximate the charge density in V_{es}, the xc energy operator, U_{xc}, and the xc potential, V_{xc}, using LCGTO expansions,

$$\begin{aligned} \rho(\mathbf{r}) &\approx \overline{\rho}(\mathbf{r}) = \sum_m f_m F_m(\mathbf{r}) \\ U_{xc}(\mathbf{r}) &\approx \overline{U}_{xc}(\mathbf{r}) = \sum_m \mathrm{u}_m G_m(\mathbf{r}) \\ V_{xc}(\mathbf{r}) &\approx \overline{V}_{xc}(\mathbf{r}) = \sum_m \mathrm{v}_m G_m(\mathbf{r}), \end{aligned} \tag{8}$$

centered primarily on the nuclei, but in which bond-centered s-type functions can be used to eliminate some high-angular-momentum nuclear-centered functions. Using these fits, the total energy expression[9],

$$\begin{aligned} E = &\sum_{k>k'} \frac{Z_k Z_{k'}}{|\mathbf{R}_k - \mathbf{R}_{k'}|} - \frac{1}{2}\sum_i \int d^3r\, n_i\, \phi_i(\mathbf{r})\nabla^2\phi_i(\mathbf{r}) \\ &- \sum_k Z_k \left\langle \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} \right\rangle + \sum_m f_m[\rho|F_m] + \sum_m \mathrm{u}_m \langle \rho G_m \rangle , \\ &- \sum_{mn} f_m f_n \frac{[F_m|F_n]}{2} \end{aligned} \tag{9}$$

is stationary with respect to variations of the molecular orbital coefficients c_{ij} and the charge density fitting coefficients, f_m, if and only if the xc fit is exact. This

requires the fitting basis set, $G_m(\mathbf{r})$, be complete. In that case the gradient of the total energy with respect to the Cartesian nuclear coordinates is relatively easy to evaluate[6-8],

$$\begin{aligned}\frac{\partial E}{\partial X_k} &= \sum_{k'\neq k} \frac{Z_k Z_{k'}(X_k - X_{k'})}{|\mathbf{R}_k - \mathbf{R}_{k'}|^3} - \sum_k Z_k \int d^3r \frac{\rho(\mathbf{r})(x - X_k)}{|\mathbf{R}_k - \mathbf{r}|^3} \\ &+ \sum_{ij}\Bigg[P_{ij}\left(-\frac{1}{2}\left\langle \chi_i^* \nabla^2 \frac{\partial \chi_j}{\partial X_k}\right\rangle - \sum_n \left\langle \chi_i^*(\mathbf{r}) \frac{\partial \chi_j(\mathbf{r})}{\partial X_k} \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|}\right\rangle\right. \\ &+ \left.\sum_m f_m[\chi_i^* \frac{\partial \chi_j}{\partial X_k}|F_m] + \sum_m \mathrm{v}_m \left\langle \chi_i^* \frac{\partial \chi_j}{\partial X_k} G_m\right\rangle\right) - \Omega_{ij}\left\langle \chi_i^* \frac{\partial \chi_j}{\partial X_k}\right\rangle + c.c.\Bigg] \\ &+ \sum_m f_m[\rho|\frac{\partial F_m}{\partial X_k}] - \sum_{mn} f_m f_n [F_n|\frac{\partial F_m}{\partial X_k}], \end{aligned} \tag{10}$$

where *c.c.* means take the complex conjugate of the previous expression within the corresponding set of parentheses. In this expression P_{ij}, is the matrix element for orbitals i and j of the one-electron density matrix,

$$P_{ij} = \sum_p n_p \sum_{ij} c_{ip}^* c_{jp}, \tag{11}$$

and Ω_{ij} is the one-electron eigenvalue weighted density matrix element

$$\Omega_{ij} = \sum_p \varepsilon_p n_p \sum_{ij} c_{ip}^* c_{jp}. \tag{12}$$

The first two terms of Eq. 10 represent the standard terms for the Hellmann-Feynman force, the next two terms represent corrections to Hellmann-Feynman arising from the dependence of the orbital basis on nuclear coordinates[1], and the last two terms represent corrections arising from fitting the charge density (Eq. 8). Expressions for third derivatives of the total energy have been obtained assuming that the xc fitting basis is complete and that the fits are exact[8].

The subject of this work is the correction term that arises from approximating U_{xc} and V_{xc}. This term has been evaluated[5] for the special case of Xα, where both U_{xc}

and V_{xc} are porportional to $\rho^{1/3}$, which can be treated using analytical integration. For all LDF's this correction term diminishes with increasing number of points and number of fitting functions used to treat U_{xc} and V_{xc}.[6,14]

III. INCOMPLETE EXCHANGE-CORRELATION FITTING BASES

In the case of an incomplete xc fitting basis set, Eq. 10 needs to be corrected by adding a term to the right-hand side of the equation,

$$\frac{\partial E^1_{xc}}{\partial X_k} = \sum_m \frac{\partial[\mathrm{u}_m \langle \rho G_m \rangle]}{\partial X_k} - \sum_{ijm} \mathrm{v}_m \frac{\partial P_{ij}}{\partial X_k} \langle \chi_i^* \chi_j G_m \rangle$$
$$- \sum_{ijm} \left(\mathrm{v}_m P_{ij} \left\langle \chi_i^* \frac{\partial \chi_j}{\partial X_k} G_m \right\rangle + c.c. \right), \tag{13}$$

The first term is the exact differentiation of the xc energy of Eq. 10, the second term comes from using the one-electron equations, Eq. 4, to eliminate all terms involving derivatives of the density matrix elements from Eq. 10, and the final term is the only apparent xc term present in Eq. 10.

Because Eq. 13 is a density functional expression, the terms involving v_m can be more compactly expressed,

$$\frac{\partial E^1_{xc}}{\partial X_k} = \sum_m \frac{\partial[\mathrm{u}_m \langle \rho G_m \rangle]}{\partial X_k} - \sum_m \mathrm{v}_m \left\langle \frac{\partial \rho}{\partial X_k} G_m \right\rangle, \tag{14}$$

and the whole expression expanded,

$$\frac{\partial E^1_{xc}}{\partial X_k} = \sum_m \frac{\partial \mathrm{u}_m}{\partial X_k} \langle \rho G_m \rangle + \sum_m \mathrm{u}_m \left\langle \rho \frac{\partial G_m}{\partial X_k} \right\rangle$$
$$+ \left\langle \frac{\partial \rho}{\partial X_k} (\overline{U}_{xc} - \overline{V}_{xc}) \right\rangle, \tag{15}$$

where the approximate quantities defined in Eq. 8 have been substituted for the

appropriate expansion. The least-squares-fit (LSF) equations for the xc energy fitting coefficients, u_m, must be differentiated to evaluate this expression.

IV. NUMERICAL INTEGRATION

In what follows we will assume that we have at our disposal a numerical integration scheme involving a set of points, $\mathbf{r}_i$ and an associated set of volume elements $\Delta\tau_i$,

$$\{f(\mathbf{r})\} = \sum_i \Delta\tau_i f(\mathbf{r}_i), \tag{16}$$

with the property that we can increase the number of points to make the numerical integral $\{f(\mathbf{r})\}$ arbitrarily close in value to the analytic integral $\langle f(\mathbf{r})\rangle$. We further assume that numerical integration is used only to fit U_{xc} and V_{xc}, via a weighted LSF scheme,

$$\sum_m \mathrm{v}_m \{W_\mathrm{v} G_m G_n\} = \{W_\mathrm{v} V_{xc} G_n\}, \tag{17}$$

$$\sum_m \mathrm{u}_m \{W_\mathrm{u} G_m G_n\} = \{W_\mathrm{u} U_{xc} G_n\}, \tag{18}$$

where the weight functions W_v and W_u are arbitrary positive (or negative) semidefinite functions of position. Eq. 18 can be inverted to give the fitting coefficients,

$$u_m = \sum_n \{W_\mathrm{u}\mathbf{GG}\}^{-1}_{mn} \{W_\mathrm{u} U_{xc} G_n\}, \tag{19}$$

where the symmetric matrix $\mathbf{GG}$ is the tensor product of the vector $\mathbf{G}$ with itself.

We now assume that we have some method for choosing the points and volume elements of Eq. 16 so that we can systematically improve the accuracy of this numerical integration, albeit at an ever increasing computational price. Therefore, we shall ignore how the weights and points of this numerical integration vary as any Cartesian nuclear coordinate changes.

Differentiating Eq. 18 gives the derivatives of the xc energy fitting coefficients,

$$\frac{\partial \mathrm{u}_m}{\partial X_k} = \sum_n \langle W_\mathrm{u}\mathbf{GG}\rangle^{-1}_{mn} \left(\left\{ W_\mathrm{u} \frac{\partial U_{xc}}{\partial X_k} G_n \right\} - \sum_p \mathrm{u}_p \left\{ W_\mathrm{u} \frac{\partial G_p}{\partial X_k} G_n \right\} \right.$$
$$\left. + \left\{ \frac{\partial W_\mathrm{u}}{\partial X_k} (U_{xc} - \overline{U}_{xc}) G_n \right\} + \left\{ W_\mathrm{u} (U_{xc} - \overline{U}_{xc}) \frac{\partial G_n}{\partial X_k} \right\} \right). \tag{20}$$

The derivatives of the xc energy fitting coefficients in Eq. 15 appear multiplied by the overlap integral of the density and the xc basis functions suggesting a new set of variables,

$$t_m = \sum_n \{W_\mathrm{u}\mathbf{GG}\}^{-1}_{mn} \langle \rho G_n \rangle, \tag{21}$$

and

$$T(\mathbf{r}) = \sum_m t_m G_m(\mathbf{r}). \tag{22}$$

Using these variables, the summation,

$$\sum_m \frac{\partial \mathrm{u}_m}{\partial X_k} \langle \rho G_m \rangle = \left\{ W_\mathrm{u} T \frac{\partial U_{xc}}{\partial X_k} \right\} - \sum_m \mathrm{u}_m \left\{ W_\mathrm{u} T \frac{\partial G_m}{\partial X_k} \right\}$$
$$+ \left\{ \frac{\partial W_\mathrm{u}}{\partial X_k} (U_{xc} - \overline{U}_{xc}) T \right\} + \sum_m t_m \left\{ W_\mathrm{u} (U_{xc} - \overline{U}_{xc}) \frac{\partial G_m}{\partial X_k} \right\}, \tag{23}$$

can be used to eliminate the derivatives of the xc energy density fitting coefficients from Eq. 15,

$$\frac{\partial E^1_{xc}}{\partial X_k} = \left\{ \frac{\partial W_\mathrm{u}}{\partial X_k} (U_{xc} - \overline{U}_{xc}) T \right\} + \sum_m t_m \left\{ W_\mathrm{u} (U_{xc} - \overline{U}_{xc}) \frac{\partial G_m}{\partial X_k} \right\}$$
$$+ \sum_m \mathrm{u}_m \left(\left\langle \rho \frac{\partial G_m}{\partial X_k} \right\rangle - \left\{ W_\mathrm{u} T \frac{\partial G_m}{\partial X_k} \right\} \right)$$
$$+ \left\langle (\overline{U}_{xc} - \overline{V}_{xc}) \frac{\partial \rho}{\partial X_k} \right\rangle - \left\{ W_\mathrm{u} T \frac{U_{xc} - V_{xc}}{\rho} \frac{\partial \rho}{\partial X_k} \right\}, \tag{24}$$

where Eq. 7 has been used to evaluate the derivative of U_{xc}.

Eqs. 21 and 22 can be rewritten,

$$\{W_{\mathrm{u}}T\mathbf{G}\} = \langle\rho\mathbf{G}\rangle. \tag{25}$$

In other words, for each weight function the corresponding T exactly transforms a numerical integral into an analytic integral on the set of functions exactly fit by the basis $\mathbf{G}$. For other functions, the transformation is into the analytic integral of the fitted quantity,

$$\{W_{\mathrm{u}}TF\} = \langle\rho\overline{F}\rangle. \tag{26}$$

In particular, this hold for the xc energy operator,

$$\{W_{\mathrm{u}}TU_{xc}\} = \langle\rho\overline{U}_{xc}\rangle, \tag{27}$$

and

$$\{W_{\mathrm{u}}TV_{xc}\} = \langle\rho\overline{V}_{xc}\rangle, \tag{28}$$

provided W_{v} is chosen to be W_{u}. These relationships are independent of the accuracy of the numerical integration scheme and requires only that the matrix $\{W_{\mathrm{u}}\mathbf{GG}\}$ be invertible. If the basis $\mathbf{G}$ is complete, then Eq. 23 vanishes identically independent of the quality of the numerical integration. Therefore, for large xc basis sets improving the numerical integration scheme might not improve the accuracy of the gradients if they are approximately computed using Eq. 10.

V. VARIATIONAL XC FITTING

It appears impossible to avoid resolving the one-electron equations to determine derivatives of ρ with respect to the nuclear coordinates that are necessary to evaluate Eq. 23 precisely when the fitting basis set is incomplete. An additional SCF

processes, analogous to the coupled-perturbed-Hartree-Fock calculation[15], can be avoided if the one-electron equations are true variations of Eq. 9. To satisfy this requirement, a variational xc potential must be defined, perhaps most directly, by considering the derivative with respect to an arbitrary one-electron occupation number,

$$\begin{aligned}\langle \phi_i^* V_{xc}^{var} \phi_i \rangle &= \frac{\partial \left\langle \rho \overline{U}_{xc} \right\rangle}{\partial n_i} \\ &= \left\langle \phi_i^* \overline{U}_{xc} \phi_i \right\rangle + \sum_m \frac{\partial u_m}{\partial n_i} \langle \rho G_m \rangle \end{aligned} \tag{29}$$

The remaining derivatives can be obtained by differentiating Eq. 18 again. This equation contains half as many terms as Eq. 24 because **G** is now assumed constant,

$$\begin{aligned}\langle \phi_i^* V_{xc}^{var} \phi_i \rangle = \left\langle \phi_i^* \overline{U}_{xc} \phi_i \right\rangle &+ \left\{ \phi_i^* T (U_{xc} - \overline{U}_{xc}) \frac{dW}{d\rho} \phi_i \right\} \\ &+ \left\{ \phi_i^* T (V_{xc} - U_{xc}) \frac{W}{\rho} \phi_i \right\}. \end{aligned} \tag{30}$$

In this equation the weight function does not contain a subscript, because the xc potential is not going to be fit. Instead the matrix elements of the xc potential,

$$\begin{aligned}\langle \chi_i^* V_{xc}^{var} \chi_j \rangle &= \left\langle \chi_i^* \overline{U}_{xc} \chi_j \right\rangle \\ &+ \left\{ \chi_i^* T \left((U_{xc} - \overline{U}_{xc}) \frac{dW}{d\rho} + (V_{xc} - U_{xc}) \frac{W}{\rho} \right) \chi_j \right\}. \end{aligned} \tag{31}$$

were obtained directly. In this expression W is taken to be a function of the density alone.

If the weight function is chosen to be unity, then summing this expression over all occupied orbitals and using Eqs. 27 and 28 gives precisely $\langle \rho \overline{V}_{xc} \rangle$, as expected.

The weight function[16],

$$W = \frac{\rho}{U_{xc}}, \tag{32}$$

that is the optimal density functional expression for computing the total energy in the nonvariational LCGTO method[9-11] has derivative

$$\frac{dW}{d\rho} = \frac{2U_{xc} - V_{xc}}{U_{xc}^2}. \tag{33}$$

The choice of weighting function, W, is less important now because the function is included in the SCF process.

Having defined a variational xc potential, the derivative of the fitted xc energy is simplified,

$$\frac{\partial \left\langle \rho \overline{U}_{xc} \right\rangle}{\partial X_k} = \left\langle \frac{\partial \rho}{\partial X_k} V_{xc}^{var} \right\rangle + \sum_m \left(\frac{\partial \mathrm{u}_m}{\partial X_k} \right)_\rho \langle \rho G_m \rangle + \sum_m \mathrm{u}_m \left\langle \rho \frac{\partial G_m}{\partial X_k} \right\rangle, \tag{34}$$

where the parentheses and subscript on the derivative of the xc energy coefficient indicates that ρ must be held constant during this partial differentiation. The first term comes from Eq. 29, and the remaining two terms come from changes in the fitting basis set, which is independent of the density. Using the variational xc potential, Eq. 31, in the one-electron secular equation, Eq. 4, eliminates all terms containing a derivative of the density (and density functional weight function) from the gradient correction term, Eq. 24. Thus the precise derivative of the total energy using a variational xc potential is

$$\begin{aligned}\frac{\partial E}{\partial X_k} = &\sum_{k' \neq k} \frac{Z_k Z_{k'} (X_k - X_{k'})}{|\mathbf{R}_k - \mathbf{R}_{k'}|^3} - \sum_k Z_k \int d^3 r \frac{\rho(\mathbf{r})(x - X_k)}{|\mathbf{R}_k - \mathbf{r}|^3} \\ &+ \sum_{ij} \Bigg[P_{ij} \left(-\frac{1}{2} \left\langle \chi_i^* \nabla^2 \frac{\partial \chi_j}{\partial X_k} \right\rangle - \sum_n \left\langle \chi_i^* \frac{\partial \chi_j}{\partial X_k} \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} \right\rangle \right. \\ &\left. + \sum_m f_m [\chi_i^* \frac{\partial \chi_j}{\partial X_k} | F_m] + \left\langle \chi_i^* \frac{\partial \chi_j}{\partial X_k} V_{xc}^{var} \right\rangle \right) - \Omega_{ij} \left\langle \chi_i^* \frac{\partial \chi_j}{\partial X_k} \right\rangle + c.c. \Bigg]\end{aligned}$$

$$+\sum_m f_m[\rho|\frac{\partial F_m}{\partial X_k}] - \sum_{mn} f_m f_n [F_n|\frac{\partial F_m}{\partial X_k}]$$

$$+\sum_m \mathrm{u}_m \left(\left\langle \rho \frac{\partial G_m}{\partial X_k}\right\rangle - \left\{ WT\frac{\partial G_m}{\partial X_k}\right\}\right) + \sum_m t_m \left\{ W(U_{xc} - \overline{U}_{xc})\frac{\partial G_m}{\partial X_k}\right\} \quad (35)$$

where

$$\left\langle \chi_i^* \frac{\partial \chi_j}{\partial X_k} V_{xc}^{var} \right\rangle = \left\langle \chi_i^* \overline{U}_{xc} \frac{\partial \chi_j}{\partial X_k} \right\rangle$$
$$+ \left\{ \chi_i^* T \left((U_{xc} - \overline{U}_{xc}) \frac{dW}{d\rho} + (V_{xc} - U_{xc}) \frac{W}{\rho} \right) \frac{\partial \chi_j}{\partial X_k} \right\}. \quad (36)$$

The price that is paid for an exact derivative is the coupling of the eigenvalue problem and numerical fitting/integration.

VI. CONCLUSION

The error terms in existing gradient LCGTO LDF programs have been analyzed. The derivatives of the fitting coefficients with respect to nuclear coordinate have been eliminated from Eq. 23, however the derivative of the density cannot be eliminated without adding an additional SCF proceedure. A better approach is to use V_{xc}^{var} in the one-electron equations. This correction replace two quasi-independent fitting proceedures, Eq. 17 and Eq. 18, with one, the latter. Thus the xc fitting basis set can be optimized to fit only the xc energy operator. Furthermore, this correction leads to directly computable gradients, Eq. 35. This derivative is exact under the assumption that the grid of points necessary to fit the xc energy density do not move with the nuclei. That is, of course, not true unless the grid leads to accurate numerical integration. Eq. 26 strongly suggests that this remaining problem will be minimized. In any event, existing grids[17] make this problem negligible, at least temporarily.

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